Electronic Supplementary Information

Cationic vacancies-accelerated the generation of CoOOH in perovskite hydroxides for the electrooxidation of biomass

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Materials Preparation

The synthesis of SnCo(OH)₆ was achieved by co-precipitation. In a typical synthesis, 2 mmol of cobalt nitrate (Co(NO₃)₂ • 6H₂O) and 2 mmol of sodium citrate (C₆H₃Na₃O₇ • 2H₂O) were dissolved in 70 mL deionized water and stirred for around half an hour. 10 mL of tin chloride (SnCl₄ • 5H₂O) solution (0.2 M) was added into the above solution dropwise under vigorous stirring for another half an hour to get a colloidal solution. The pH was tuned to about 10 by drop-wise addition of 10 mL of NaOH solution (2 M). The precipitates were collected by centrifuging at 8000 rpm for 10 min, then washed with deionized water and ethanol three times. The obtained precipitation was finally dried overnight in a vacuum oven. The SnCo(OH)₆ with Sn vacancies (SnCo(OH)₆-V_{Sn}) was prepared by Ar plasma. The specific treatment steps were listed as follows: A layer of SnCo(OH)₆ powder was placed on a quartz boat and put into a tube plasma-treatment instrument. Then argon gas was flushed at a flow rate of 25 sccm for 5 minutes to remove air from the tube. After that, the argon gas flow rate was adjusted to 8 sccm, and the plasma power was set to 200 W. The treatment time was 8 minutes. After the treatment, the instrument was turned off, to let the argon gas flushed slowly till the tube cool down. Finally, the SnCo(OH)_{6-Vsn} powder was obtained.

Characterization

The TEM characterization was performed on a Titan G260-300. The XRD characterization was conducted on a Bruker D8 Advance diffractometer. The BET test was measured by a Micromeritics ASAP 2020 V3.02 H. The XPS was taken using a SHIMADZU-KRATOS, AXIS SUPRA. The XANES test was performed at TLS-BL17C at the National Synchrotron Radiation Research Center, Taiwan. The EPR test was taken using a JES-FA 200.

Electrochemical measurements

All the electrochemical measurements were performed with a CHI 760e electrochemical analyzer. Unless noted otherwise, the as prepared catalyst was directly used as the working electrode in all the tests in the three-electrode cell. In contrast, a graphite rod was used as the counter electrode, and Hg/HgO (1 M KOH) electrode was used as the reference electrode. LSV was measured with the scan

rate of 5 mV \cdot s⁻¹ in an undivided cell, and a constant potential electrolysis test was measured in a divided cell (separated by Nafion 117 membrane). In operando electrochemical impedance spectroscopy (EIS) tests were measured over a frequency range from 10⁵ to 10⁻² Hz with an AC amplitude of 10 mV. Except for the EIS, agitation was maintained throughout all electrochemical tests.

HPLC analysis

HPLC (Shimadzu Prominence LC-20AT system) was equipped with an ultraviolet-visible detector to analyze HMF oxidation products. Specifically, 40 μ L of electrolyte was removed during potentiostatic electrolysis, diluted to 2 mL with ultrapure water, and analyzed it by HPLC. The specific parameters were set as follows. The wavelength of the UV detector was set to 265 nm, mobile phase A was methanol and phase B was 5 mM ammonium formate aqueous solution. The ratio of A:B was 1:9, and the flow rate was 0.9 mL min⁻¹. Using a 4.6 mm×150 mm Shim-pack GWS 5 μ m C18 column, each separation lasted for 17 minutes.

The HMF conversion, FDCA yield and faradaic efficiency were calculated using equations (1), (2) and (3), respectively.

HMF conversion (%) = (n(HMF consumed) / n(HMF initial)) \times 100		(1)
FDCA yield (%) = (n(FDCA formed) / n(HMF initial)) \times 100	(2)	
Faradaic efficiency (%) = (n(FDCA formed) / Charge) $\times 6 \times F \times 100$		(3)

Where F is the Faraday constant (96,485 C mol⁻¹), and n is the mol of reactant calculated from the concentration measured by HPLC.

Computational detail

This study used the VASP program to perform spin-polarized DFT calculations ^{1,2}. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and PAW method were used to describe the exchangecorrelation and ionic cores, respectively ^{3,4}. According to XRD results, (100) surface was chosen as the study surface for both $SnCo(OH)_6$ and $SnCo(OH)_6$ - V_{Sn} . We used a 2 × 2 × 1 supercell, 2 × 2 × 1 Gamma K point mesh for the Brillouin zone integration, and a vacuum layer of 15 Å to prevent interactions between periodic images of the slab. The Hubbard + U approach was employed to alleviate the delocalization error of GGA functional for treating transition metal atoms. Based on the U-J value in the literature, 3.3 eV was chosen for Co atom ^{5,6}. The convergence tolerance for energy and force was set to 1×10^{-5} eV/cell and 0.05 eV/Å, respectively. Analysis of the output data from VASP, visualization of atomic structure and electronic results, etc., were achieved through the VASPKIT tool ⁷.

The Part of Supporting Fig.s



Fig. S2 (a) SEM and (c) TEM images of $SnCo(OH)_6$; (d) SEM and (f) TEM images of $SnCo(OH)_6$ - V_{Sn} . Particle size distributions of (b) $SnCo(OH)_6$ and (e) $SnCo(OH)_6$ - V_{Sn} .



Fig. S3 (a) Sn 3d, (b) Co 2p, (c) O 1s XPS spectra of SnCo(OH)₆ and SnCo(OH)₆-V_{Sn}.In Sn 3d spectrum, the peak at 486.4 eV corresponds to Sn⁴⁺. In Co 2p spectrum, the peak at 780.6 eV corresponds to Co²⁺, and two peaks at 782.1 eV and 786.1 eV correspond to satellite peaks. In the O 1s spectrum, two peaks at 530.9 eV and 531.8 eV correspond to metal-OH bonds and adsorbed H₂O.



Fig. S4 (a) The Co *K*-edge XANES spectra of $SnCo(OH)_6$ and $SnCo(OH)_6$ -V_{Sn}; (b) The Sn *K*-edge XANES spectra of $SnCo(OH)_6$ and $SnCo(OH)_6$ -V_{Sn}.



Fig. S5 (a)The Co *K*-edge XANES spectra of $SnCo(OH)_6$, $SnCo(OH)_6$ - V_{Sn} , and standard Co foil, Co_3O_4 , and CoO; (b) The Sn *K*-edge XANES spectra of $SnCo(OH)_6$, $SnCo(OH)_6$ - V_{Sn} , and standard SnO_2 , Sn foil.



Fig. S6 Electrochemically active surface area (ECSA) tests in 1 M KOH. Cyclic voltammetry (CV) curves of (a) $SnCo(OH)_6$ and (b) $SnCo(OH)_6$ - V_{Sn} with different scanning rates; (c) The C_{dl} of $SnCo(OH)_6$ and $SnCo(OH)_6$ - V_{Sn} .



Fig. S7 (a) The N₂ adsorption-desorption isotherms of $SnCo(OH)_6$ and $SnCo(OH)_6$ -V_{Sn}; (b) The pore size distribution of $SnCo(OH)_6$ and $SnCo(OH)_6$ -V_{Sn}.



Fig. S8 (a, b) The HMFOR performance of $SnCo(OH)_6$ and $SnCo(OH)_6$ -V_{Sn} after BET and ECSA normalization.



Fig. S9 (a) HPLC measurements of pure FDCA, HMF, FFCA, HMF, DFF, and (b-f) their standard curve line.



Fig. S10 The equivalent circuit is used for modeling the measured electrochemical response. R_s stands for the solution resistance, CPE represents double-layer capacitance, and R_{ct} has contact with the interfacial charge transfer reaction.



Fig. S11 (a, b) The Nyquist plots of $SnCo(OH)_6$ without or with 50 mM HMF at various applied potentials.



Fig. S12 (a, b) The Nyquist plots of $SnCo(OH)_6$ - V_{Sn} without or with 50mM HMF at various applied potentials.



Fig. S13 CV tests of $SnCo(OH)_6$ and $SnCo(OH)_6$ -V_{Sn} in 1 M KOH.



Fig. S14 XPS spectra of (a) SnCo(OH)₆ and (b) SnCo(OH)₆-V_{Sn} at various applied potentials.



Fig. S15 (a) Sn 3d, (b) Co 2p, (c) O 1s XPS spectra of SnCo(OH)₆-V_{Sn} at various applied potentials.



Fig. S16 (a) Sn 3d, (b) Co 2p, (c) O 1s XPS spectra of SnCo(OH)₆ at various applied potentials.



Fig. S17 The Co *R*-space of CoO, Co(OH)₂ and SnCo(OH)₆ at different reaction potentials.



Fig. S18 The HPLC chromatogram traces of the various products during the electrochemical oxidation of HMF at 1.47 V_{RHE} in 1 M KOH with 10 mM HMF for (a) $SnCo(OH)_6$ and (b) $SnCo(OH)_6$ - V_{Sn} .



Fig. S19 Concentration changes of HMF and its oxidation products during the electrochemical oxidation of HMF at 1.47 V_{RHE} in 1 M KOH with 10 mM HMF for SnCo(OH)₆.

The Part of Supporting Tables

Potential (V _{RHE})	R _s	R _{ct}	R _{ct} CPE-T	
1.15	6.591		0.00053457	0.85891
1.2	6.153		0.00047821	0.86828
1.25	5.978		0.00051778	0.8789
1.3	5.871		0.00069329	0.89182
1.35	5.811		0.0010477	0.90183
1.4	5.791		0.0018081	0.89803
1.45	5.801		0.0026166	0.90942
1.5	5.723	2285	0.0030884	0.92037
1.55	5.777	121.8	0.0034277	0.93369
1.6	6.4	17.45	0.0035471	0.9141
1.65	8.579	7.446	0.0036205	0.85631

Table S1. The resistance of each component for SnCo(OH)₆ in 1 M KOH.

Table S2. The resistance of each component for $SnCo(OH)_6$ in 1 M KOH with 50 mM HMF.

Potential	р	R CPE_T		CDE D	
(V_{RHE})	K _s	K _{ct}	CPE-1	CPE-P	
1.15	5.475	44897	0.0002757	0.81657	
1.2	5.414	34820	0.00028478	0.81541	
1.25	5.296	19994	0.00032651	0.82493	
1.3	5.586	7610	0.00049072	0.82399	
1.35	5.84	2096	0.00097253	0.82774	
1.4	5.879	954.9	0.0018083	0.82244	
1.45	5.995	574.7	0.0026534	0.83165	
1.5	5.889	270	0.0031843	0.82983	
1.55	6.092	114.8	0.0035433	0.82291	
1.6	6.39	29.84	0.0031593	0.88002	
1.65	8.007	11.29	0.0031922	0.8279	
Table S3. The resistance of each component for SnCo(OH) ₆ -V _{Sn} in 1 M KOH.					
Potential (V _{RHE})	R _s	R _{ct}	CPE-T	CPE-P	
1.15	7.409		0.0018741	0.85464	

1.2	7.051		0.0016307	0.89304
1.25	7.406		0.0018009	0.91175
1.3	7.873		0.0023359	0.91951
1.35	7.687		0.0032367	0.91762
1.4	7.982		0.0046862	0.90072
1.45	7.96	7246	0.0058045	0.88987
1.5	7.899	543.9	0.0060347	0.89541
1.55	8.249	84.9	0.0057835	0.88817
1.6	8.831	21.48	0.0052255	0.88096
1.65	9.741	10.58	0.0060142	0.79204

Table S4. The resistance of each component for $SnCo(OH)_6$ - V_{Sn} in 1 M KOH with 50 mM HMF.

Potential (V _{RHE})	R _s	R _{ct}	CPE-T	CPE-P
1.15	8.878	11380	0.0029707	0.88022
1.2	8.587	4760	0.0024052	0.89192
1.25	8.256	1814	0.0023649	0.88763
1.3	7.925	735.7	0.0026757	0.88391
1.35	7.771	364.4	0.0032449	0.88012
1.4	7.668	245.3	0.0040317	0.87633
1.45	7.491	187.4	0.0048154	0.8532
1.5	7.327	150.4	0.0051937	0.83531
1.55	7.392	93.94	0.0051876	0.81518
1.6	7.289	36.98	0.0046479	0.83662
1.65	7.344	14.32	0.0047385	0.81888

Table S5. The structural parameters of $SnCo(OH)_6$ extracted from the EXAFS fitting.

Potential (V _{RHE})	Path	CN	R(Å)	σ ² (×10 ⁻³ Å ²)	$\Delta E_0 (eV)$	R factor
OCP	Со-ОН	5.03	2.096	0.00711	-6.986	0.014
1.15	Со-ОН	4.98	2.098	0.00687	-6.827	0.015
1.20	Со-ОН	5.02	2.095	0.00684	-7.107	0.013
1.40	Со-ОН	5.09	2.095	0.00724	-7.146	0.013
1.45	Со-ОН	4.94	2.095	0.00668	-7.087	0.011
1.65	Со-ОН	5.01	2.096	0.00682	-6.977	0.014

Potential (V _{RHE})	Path	CN	R(Å)	σ ² (×10 ⁻³ Å ²)	$\Delta E_0 (eV)$	R factor
OCP	Со-ОН	5.53	2.058	0.01487	-8.719	0.010
1.15	Со-ОН	5.86	2.090	0.01672	-6.339	0.022
1.20	Со-ОН	5.64	2.106	0.01704	-4.268	0.032
1.30	Co-O	4.91	2.102	0.01411	-4.289	0.013
1.40	Co-O	4.80	2.016	0.01395	-3.627	0.011
1.45	Co-O	4.79	2.111	0.01462	-3.389	0.013
1.65	Co-O	5.05	2.106	0.01744	-3.101	0.021

Table S6. The structural parameters of $SnCo(OH)_6$ -V_{Sn} extracted from the EXAFS fitting.

Table S7. The comparison of activity for $SnCo(OH)_6$ - V_{Sn} and other reported catalysts.

Catalvete	Potential at a current	Advance	FDCA	References
	density of 10 mA cm ⁻²	potential	yield	Kelefelices
P-SnCo(OH) ₆	1.41 V	200 mV	94.7%	This work
Pristine SnCo(OH) ₆	1.61 V	200 m v	76.4%	This work
Vo-Co ₃ O ₄	1.35 V	90 mV	91.9%	8
CuCo ₂ O ₄	~1.40 V	180 mV	93.7%	9
NiCo ₂ O ₄	$\sim 1.47 \ V$	-	90.4%	10
F doped NiCo ₂ O ₄	~ 1.38 V	40 mV	$\sim 82\%$	11
NiCoFe LDH	1.52 V	58 mV	84.9%	12
NiCoMn LDH	~1.52 V	-	91.7%	13
CoAl LDH NSA	1.30 V	100 mV	~95%	14
d-NiFe LDH/CP	$\sim 1.47 \ V$	50 mV	96.8%	15
NF@Co ₃ O ₄ /CeO ₂	~ 1.34 V	40 mV	94.5%	16
(FeCrCoNiCu) ₃ O ₄	~ 1.52 V	-	97.4%	17
Ce-CoP	~1.30 V	350 mV	98%	18
CoO-CoSe ₂	~1.33 V	190 mV	99%	19
Vo-Co ₃ O ₄	1.54 V	28 mV	~60%	20
Vo-NiO	~1.34 V	140 mV	99.2%	21

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